



December 19, 2001

BOX PCT

Commissioner for Patents
Washington, D.C. 20231

PCT/JP00/04239
-filed June 28, 2000

Re: Application of Hideya SAITO, Tetsuya HIGUCHI, Satoshi KOMATSU and
Takayuki TANAKA
FLUORINE-CONTAINING ELASTOMER AND VULCANIZED MOLDED
ARTICLE
Assignee: DAIKIN INDUSTRIES, LTD.
Our Ref: Q67396

Dear Sir:

The following documents and fees are submitted herewith in connection with the above application for the purpose of entering the National stage under 35 U.S.C. § 371 and in accordance with Chapter II of the Patent Cooperation Treaty:

- an executed Declaration and Power of Attorney.
- an English translation of the International Application.
- an English translation of Article 34 amendments
- an executed Assignment and PTO 1595 form.
- Notification Concerning Submission or Transmittal of Priority Document
- International Search Report, Information Disclosure Statement and PTO 1449 form
- a Preliminary Amendment

It is assumed that copies of the Articles 19 and 34 amendments as required by § 371(c) will be supplied directly by the International Bureau, but if further copies are needed, the undersigned can easily provide them upon request.

The Government filing fee, after entry of the Article 34 Amendment and Preliminary Amendment, is calculated as follows:

| | | | | | | | |
|--------------------|-----------|---|-----------|---|-------|-------------|----------|
| Total claims | <u>14</u> | - | <u>20</u> | = | _____ | x \$18.00 = | \$0.00 |
| Independent claims | <u>1</u> | - | <u>3</u> | = | _____ | x \$84.00 = | \$0.00 |
| Base Fee | | | | | | | \$890.00 |

| | |
|----------------------------------|------------------------|
| TOTAL FILING FEE | <u>\$890.00</u> |
| Recordation of Assignment | <u>\$ 40.00</u> |
| TOTAL FEE | <u><u>\$930.00</u></u> |

10/018367

JC13 Rec'd PCT/PTO 19 DEC 2001



SUGHRUE MION, PLLC

Q67396

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Checks for the statutory filing fee of \$890.00 and Assignment recordation fee of \$40.00 are attached. You are also directed and authorized to charge or credit any difference or overpayment to Deposit Account No. 19-4880. The Commissioner is hereby authorized to charge any fees under 37 C.F.R. §§ 1.16, 1.17 and 1.492 which may be required during the entire pendency of the application to Deposit Account No. 19-4880. A duplicate copy of this transmittal letter is attached.

Priority is claimed from:

| <u>Country</u> | <u>Application No</u> | <u>Filing Date</u> |
|----------------|-----------------------|--------------------|
| Japan | 183676/1999 | June 29, 1999 |
| Japan | 2000-86667 | March 27, 2000 |

Respectfully submitted,

A handwritten signature in black ink, appearing to read "AJR".

Abraham J. Rosner
Registration No. 33,276

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Date: December 19, 2001

PATENT APPLICATION**IN THE UNITED STATES PATENT AND TRADEMARK OFFICE**

In re application of

Hideya SAITO, et al.

Appln. No.: National Stage Entry of PCT/JP00/04239

Confirmation No.: NOT YET ASSIGNED

Group Art Unit: NOT YET ASSIGNED

Filed: December 19, 2001

Examiner: NOT YET ASSIGNED

For: FLUORINE-CONTAINING ELASTOMER AND VULCANIZED MOLDED ARTICLE

PRELIMINARY AMENDMENT

Commissioner for Patents
Washington, D.C. 20231

Sir:

In the Article 34 Amendment, please renumber pages 35 and 36 as pages 36 and 37, respectively. In the specification, please renumber page 39 (Abstract) as page 38.

Prior to examination, and following entry of the Article 34 Amendment, please amend the above-identified application as follows:

IN THE CLAIMS:

Please enter the following amended claims:

9. (Twice amended) The fluorine-containing elastomeric terpolymer of Claim 1, wherein a number average molecular weight of the terpolymer is from 5,000 to 500,000 based on polystyrene.

10. (Twice amended) A composition for vulcanization which comprises the fluorine-containing elastomeric terpolymer of Claim 1 and a vulcanizing agent.

PRELIMINARY AMENDMENT - Q67396

12. (Amended) The composition of Claim 10, wherein the vulcanizing agent is a polyol vulcanizing agent.
13. (Amended) A vulcanized molded article produced by molding and vulcanizing the composition for vulcanization of Claim 10.

Please add the following new claims:

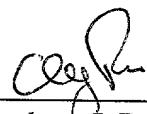
15. (New) The composition of Claim 10, wherein the fluorine-containing elastomeric terpolymer is the fluorine-containing elastomeric terpolymer of Claim 8.
16. (New) The composition of Claim 15, which contains a vulcanization accelerator.
17. (New) The composition of Claim 15, wherein the vulcanizing agent is a polyol vulcanizing agent.
18. (New) A vulcanized molded article produced by molding and vulcanizing the composition for vulcanization of Claim 15.
19. (New) The vulcanized molded article of Claim 18, which is used for parts for oil seal.

PRELIMINARY AMENDMENT - Q67396

REMARKS

Entry and consideration of this Amendment is respectfully requested.

Respectfully submitted,



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Date: December 19, 2001

PRELIMINARY AMENDMENT - Q67396

APPENDIX
VERSION WITH MARKINGS TO SHOW CHANGES MADE

IN THE CLAIMS:

The claims are amended as follows:

9. (Twice amended) The fluorine-containing elastomeric terpolymer of [any of Claims 1, 5 and 8] Claim 1, wherein a number average molecular weight of the terpolymer is from 5,000 to 500,000 based on polystyrene.

10. (Twice amended) A composition for vulcanization which comprises the fluorine-containing elastomeric terpolymer of [any of Claims 1, 5, 8 and 9] Claim 1 and a vulcanizing agent.

12. (Amended) The composition of Claim 10 [or 11], wherein the vulcanizing agent is a polyol vulcanizing agent.

13. (Amended) A vulcanized molded article produced by molding and vulcanizing the composition for vulcanization of [any of Claims 10 to 12] Claim 10.

Claims 15-19 are added as new claims.

DESCRIPTION

FLUORINE-CONTAINING ELASTOMER

AND VULCANIZED MOLDED ARTICLE

5

TECHNICAL FIELD

The present invention relates to a novel fluorine-containing elastomeric terpolymer (fluorine-containing rubber), a composition for vulcanization prepared therefrom, and a vulcanized molded article such 10 as parts for oil seal.

BACKGROUND ART

Fluorine-containing elastomers (fluorine-containing rubbers) such as vinylidene fluoride (VdF)/hexafluoropropylene (HFP) copolymer 15 and VdF/HFP/tetrafluoroethylene (TFE) copolymer have been used as starting materials for various parts in the fields where severe conditions such as high temperature and exposure to various chemicals are demanded, for example, in the fields of automotive industry, aircraft industry, semiconductor industry, etc. because of excellent heat 20 resistance, chemical resistance, oil resistance, and the like thereof.

In those fields of industries, major applications of the fluorine-containing rubbers are a sealing material and hose material for automotive-related equipment. Particularly rubber materials which are used for parts to be subject to exposure to engine oil are required to have 25 not only heat resistance and oil resistance but also chemical resistance (amine resistance) to amine compounds, etc. which are added as a stabilizer to engine oil, ATF and differential gear oil. In recent years

engine oil, ATF and differential gear oil are required to stand severer conditions as a result of demands for fuel saving and high performance of motor car. Therefore there is a tendency that an adding amount of the amine compounds, etc. is increasing, and conventional fluorine-containing rubbers as mentioned above cannot satisfy such requirements.

In such a situation, attention has been given to an elastomeric copolymer of ethylene (E)/HFP as a fluorine-containing rubber having amine resistance. The E/HFP copolymer has mechanical properties equal to those of conventional fluorine-containing rubbers and also heat resistance, solvent resistance and oil resistance approximate to those of conventional fluorine-containing rubbers.

It is expected that the fluorine-containing rubber prepared from the E/HFP copolymer is used effectively as various parts for motor car engine, transmission, chassis, etc. by utilizing the above-mentioned properties.

Typical examples of parts for engine system are those mentioned below.

(Parts for engine proper)

20 Gaskets:

Cylinder head gasket, cylinder head cover gasket, oil packing, timing belt cover gasket, etc.

Engine oil seals:

O-ring, packing, etc.

25 Hoses for engine proper:

Control hose, etc.

Others:

Power piston packing, seal for cylinder liner, etc.

(Parts for shaft)

Crank shaft seal, cam shaft seal, etc.

(Parts for valve)

5 Valve stem oil seal, etc.

(Parts for engine oil cooler)

Engine oil cooler hose, oil return hose, seal gasket, etc.

(Parts for vacuum pump)

Vacuum pump oil hose, etc.

10 (Parts for fuel pump)

Oil seal, diaphragm, valve, etc. for fuel pump

(Parts for fuel hose)

Filler (neck) hose, fuel feeding hose, fuel return hose, vapor (evaporation) hose, vent (breather) hose, etc.

15 (Parts for fuel tank)

In-tank hose, filler seal, tank packing, in-tank fuel pump mount, etc.

(Parts for fuel tube)

Fuel tube, O-ring for connector of fuel tube, etc.

20 (Parts for fuel injection system)

Injector cushion ring, injector seal ring, injector O-ring, pressure regulator diaphragm for fuel injection system, etc.

(Parts for carburetor)

25 Valve of needle valve, piston packing of acceleration pump, flange gasket, control hose for carburetor, diaphragm for sensor of carburetor, etc.

(Parts for composite air control system)

Valve seat for composite air control system, diaphragm for composite air control system, etc.

(Parts for manifold)

Suction manifold packing, exhaust manifold packing, etc.

5 (Parts for exhaust gas recirculation system)

Diaphragm for exhaust gas recirculation system, control hose for exhaust gas recirculation system, etc.

(Parts for BPT)

Diaphragm, etc.

10 (Parts for after burner)

Valve seat for prevention of after burning, etc.

(Parts for throttle)

Throttle body packing, etc.

(Parts for turbo charger)

15 Turbo oil feeding hose, turbo oil return hose, turbo air hose, inter cooler hose for turbo charger, turbine shaft seal for turbo charger, etc.

(Others)

Power piston packing, cylinder liner seal, etc.

20 Typical examples of parts for transmission system are those mentioned below.

(Parts for transmission)

Bearing seal, oil seal, O-ring, packing, etc. for transmission, hose for torque converter, etc.

25 (Parts for automatic torque converter (AT))

Transmission oil seal, ATF oil seal, O-ring, packing and front pump seal for AT, etc.

Typical examples of parts for chassis are those mentioned below.

(Parts for steering)

Power steering oil hose, etc.

5 (Parts for break oil hose)

Hose, oil seal, O-ring, packing, etc. for break oil.

(Parts for Master vac for break system)

Air valve, vacuum valve, diaphragm, etc. for Master vac.

(Parts for master cylinder for break system)

10 Piston cap (rubber cap), etc. for master cylinder.

(Parts for caliper)

Caliper seal, etc.

(Parts for boot)

Boot, etc.

15 Further examples of other parts are, for instance, wheel bearing seal, gear box oil seal, differential oil seal, pinion seal, rear axle pinion seal, universal joint gasket, speed meter pinion seal, O-ring and oil seal for torque transmission, twin carburetor tube, etc.

When the E/HFP copolymer is used for producing a molded article, the copolymer must be subjected to vulcanizing. This is the same as in usual rubbers. While various vulcanization methods are known, in case of many fluorine-containing rubbers containing a VdF unit, polyol vulcanization in which a VdF unit is used as a cure site is adopted most since processability is excellent and an obtained molded article has a good compression set. Peroxide vulcanization to be carried out by employing a peroxide is also adopted, but since there is much staining of a metal die at molding, its use is limited to a specific case. In

addition, as the case demands, polyamine vulcanization to be carried out by employing diamine is also adopted.

Journal of The Chemical Society of Japan, 1980 (1), pg. 112 describes that the E/HFP copolymers cannot be subjected to polyol 5 vulcanization and are obliged to be subjected to peroxide vulcanization. This is because the polyol vulcanization cannot be carried out since the E/HFP copolymers substantially do not have a moiety (for example, the above-mentioned VdF unit) which is easily subject to attack of a nucleophilic reagent and is capable of becoming a cure site for the polyol 10 vulcanization. On the other hand this feature gives an excellent amine resistance to the E/HFP copolymer.

In JP-A-6-248027, consideration is taken into a polyol vulcanization system which is capable of polyol vulcanization, has an amine resistance, and comprises 2 to 25 % by mole of ethylene (E), 16 to 15 30 % by mole of hexafluoropropylene (HFP) and 47 to 80 % by mole of vinylidene fluoride (VdF), and a terpolymer containing an increased amount of a VdF unit is proposed.

However studies made by the inventors of the present invention have made it clear that due to too large amount of VdF unit or 20 too small amount of ethylene unit, such a terpolymer cannot sufficiently cope with the above-mentioned severer conditions during use thereof, particularly the amine resistance.

The inventors of the present invention have made intensive studies to obtain a fluorine-containing copolymer which can be 25 subjected to polyol vulcanization and has necessary and sufficient amine resistance while maintaining heat resistance, oil resistance and chemical resistance nearly equal to those of conventional fluorine-

containing rubbers, and as a result have found that the terpolymer obtained by copolymerizing ethylene, hexafluoropropylene and vinylidene fluoride in a specific ratio has elastomeric property and satisfies the above-mentioned characteristics, and have completed the present
5 invention.

DISCLOSURE OF INVENTION

Namely the present invention relates to the fluorine-containing elastomeric terpolymer of 10 to 85 % by mole of ethylene unit,
10 14.9 to 50 % by mole of hexafluoropropylene (HFP) unit and 0.1 to 45 % by mole of vinylidene fluoride (VdF) unit.

Also the present invention relates to the fluorine-containing elastomeric terpolymer of 27 to 40 % by mole of ethylene unit, more than 45 % by mole and not more than 58 % by mole of vinylidene fluoride unit
15 and the residual amount less than 28 % by mole of hexafluoropropylene unit.

A composition for vulcanization can be prepared by adding a vulcanizing agent and as the case demands, a vulcanization accelerator to those fluorine-containing elastomeric terpolymers. A preferable
20 vulcanizing agent is a polyol vulcanizing agent.

The present invention also relates to the vulcanized molded article, for example, an oil seal which is obtained by molding and vulcanizing the composition for vulcanization.

25 BEST MODE FOR CARRYING OUT THE INVENTION

One of the fluorine-containing elastomeric terpolymers of the present invention contains 10 to 85 % by mole of ethylene unit, 14.9 to

50 % by mole of HFP unit and 0.1 to 45 % by mole of VdF unit, preferably 10 to 65 % by mole of ethylene unit, 15 to 45 % by mole HFP unit and 0.1 to 45 % by mole of VdF unit. When an amount of the ethylene unit is too large, oil resistance is lowered and when the amount is too small, 5 flexibility at low temperature (hereinafter referred to as "low temperature flexibility") is lowered. The amount of ethylene unit is preferably from 10 to 65 % by mole, particularly 30 to 65 % by mole. When the amount of HFP is too large, low temperature flexibility is lowered, and when the amount is too small, elastomeric property is lost and the terpolymer 10 becomes in the form of resin. The amount of VdF unit is preferably from 5 to 45 % by mole, particularly 20 to 45 % by mole. When the amount of VdF unit is not more than 5 % by mole, cure sites for polyol vulcanization decrease and it is difficult to carry out the polyol vulcanization only. When the amount of VdF unit is more than 0.1 % 15 by mole, vulcanization and molding can be carried out by the polyol vulcanization together with peroxide vulcanization. Also when the amount of VdF unit is more than 5 % by mole, the polyol vulcanization can be carried out solely. In order to enhance vulcanizability of polyol vulcanization, it is preferable to increase the amount of VdF unit to 20 % 20 by mole or more. When the amount of VdF unit is more than 45 % by mole, amine resistance is lowered.

When considering amine resistance most and maintaining compatibility with vulcanizability of polyol vulcanization, it is preferable that the amount of VdF unit is from 5 to 35 % by mole, particularly 5 to 25 % by mole.

In order to attach importance to amine resistance and give necessary and sufficient vulcanizability of polyol vulcanization, the

above-mentioned proportion range is proper. Particularly from the viewpoint of good balance between the amine resistance and the vulcanizability of polyol vulcanization, it is preferable that the proportion of ethylene/HFP/VdF (% by mole ratio, hereinafter the same) 5 is 20 to 50/20 to 40/28 to 42.

When the vulcanizability of polyol vulcanization is increased and processability is enhanced even if the amine resistance is somewhat sacrificed, it is possible to use a fluorine-containing elastomeric terpolymer containing more than 45 % by mole of VdF unit, namely a 10 novel copolymer of ethylene/HFP/VdF in a proportion of 27 to 40/14.9 to 28/more than 45 and not more than 58.

When attaching importance to low temperature flexibility, namely when the ethylene content is more than 65 % by mole and not more than 85 % by mole, it is preferable that the HFP unit is from 14.9 to 15 35 % by mole and the VdF unit is from 0.1 to 20 % by mole.

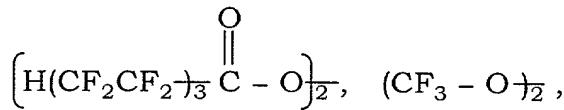
The fluorine-containing elastomeric terpolymer of the present invention can be prepared by usual radical polymerization method. The polymerization can be carried out by any of emulsion polymerization, suspension polymerization, solution polymerization and bulk 20 polymerization. Among them, emulsion polymerization and suspension polymerization are advantageous since the polymerization is carried out industrially easily and a high molecular weight polymer is easily obtained.

Examples of the radical polymerization initiator which can be 25 used for the radical polymerization are, for instance, an organic or inorganic peroxide, persulfate, azo compound, and the like.

Examples of the organic peroxide are, for instance, dialkyl

peroxides such as 2,5-dimethyl-2,5-bis(t-butylperoxy)hexane and di-t-butyl peroxide; diacyl peroxides such as isobutyl peroxide, 3,5,5-trimethylhexanoyl peroxide, octanoyl peroxide, lauroyl peroxide, stearoyl peroxide and succinic acid peroxide; peroxy dicarbonates such as dinormalpropyl peroxydicarbonate, diisopropyl peroxydicarbonate, bis(4-t-butylcyclohexyl) peroxydicarbonate, di-2-ethoxyethyl peroxydicarbonate, di-2-ethylhexyl peroxydicarbonate and di-2-methoxybutyl peroxydicarbonate; peroxy esters such as 1,1,3,3-tetramethylbutyl peroxyneodecanoate, 1-cyclohexyl-1-methylethyl peroxyneodecanoate, t-hexyl peroxyneodecanoate, t-butyl peroxyneodecanoate, t-hexyl peroxyppyvalate, t-butyl peroxyppyvalate, 1,1,3,3-tetramethylbutyl peroxy-2-ethylhexanoate, 2,5-dimethyl-2,5-bis(2-ethylhexanoylperoxy)hexane, 1-cyclohexyl-1-methylethylperoxy-2-ethylhexanoate, t-hexylperoxy-2-ethylhexanoate, t-butylperoxy-2-ethylhexanoate, t-butylperoxy isobutyrate, t-hexylperoxyisopropyl monocarbonate, t-butylperoxy-3,5,5-trimethylhexanoate, t-butylperoxy laurate, t-butylperoxyisopropyl monocarbonate, t-butylperoxy-2-ethylhexyl monocarbonate and t-butylperoxy acetate;

20



and the like.

Example of the inorganic peroxide is, for instance, hydrogen peroxide.

Examples of the persulfate are, for instance, ammonium persulfate, sodium persulfate, potassium persulfate, and the like.

In case of peroxide and persulfate, the initiator can be used in combination with a reducing agent. Examples of the reducing agent are, for instance, sodium, potassium or ammonium salt of sulfuric acid, hyposulfurous acid, pyrosulfurous acid, dithionous acid, thiosulfurous acid, phosphorous acid or hydrophosphorous acid; metal compounds to be easily oxidized such as ferrous salt, cuprous salt and silver salt; and the like.

Examples of the azo compounds are, for instance, cyano-2-propyl azoformamide, 1,1'-azobis(cyclohexane-1-carbonitrile), 2,2'-azobis(2-amidinopropane)dihydrochloride, 2,2'-azobis(2-methylbutyronitrile), 2,2'-azobisisobutyronitrile, 2,2'-azobis(2,4-dimethylvaleronitrile), 2,2'-azobis[N-(2-propenyl)-2-methylpropionamide], macro azo compound containing polydimethylsiloxane segment, 2,2'-azobis(2,4,4-trimethylpentane), 2,2'-azobis(4-methoxy-2,4-dimethylvaleronitrile), 4,4'-azobis(4-cyanovaleate), dimethyl 2,2'-azobis(isobutyrate), 2,2'-azobis[2-(2-imidazoline-2-yl)propane]dihydrochloride, 2,2'-azobis[2-(2-imidazoline-2-yl)propane]disulfate dihydrate, 2,2'-azobis[2-(2-imidazoline-2-yl)propane], 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)-2-hydroxyethyl]propionamide}, 2,2'-azobis{2-methyl-N-[1,1-bis(hydroxymethyl)ethyl]propionamide}, 2,2'-azobis[2-methyl-N-(2-hydroxyethyl)propionamide], 2,2'-azobisisobutylamide dihydrate, 2,2'-azobis[2-(hydroxymethyl)propionitrile], and the like.

An amount of the radical polymerization initiator is from 0.001 to 10 % by weight, preferably 0.01 to 5 % by weight on the basis of a total amount of the monomers.

In the preparation process of the present invention, a method

of iodine transfer polymerization (cf. JP-A-53-125491) can also be used.

In that case, when the polymerization is carried out in the presence of a compound represented by the formula (I):

5



wherein R is a saturated or un-saturated divalent fluoro hydrocarbon group or divalent chlorofluoro hydrocarbon group having 1 to 16 carbon atoms or a saturated or un-saturated divalent hydrocarbon group
10 having 1 to 3 carbon atoms, each of x and y is 0, 1 or 2, $x + y = 2$, it is advantageous because a polymerization rate is increased.

Examples of the compound represented by the formula (I) are, for instance, 1,3-diiodoperfluoropropane, 1,3-diido-2-chloroperfluoropropane, 1,4-diiodoperfluorobutane, 1,5-diido-2,4-dichloroperfluoropentane, 1,6-diiodoperfluorohexane, 1,8-diiodoperfluoroctane, 1,12-diiodoperfluorododecane, 1,16-diiodoperfluorohexadecane, diiodomethane, 1,2-diidoethane, 1,3-diido-n-propane, CF_2Br_2 , $BrCF_2CF_2Br$, $CF_3CFBrCF_2Br$, $CFClBr_2$, $BrCF_2CFClBr$, $CFBrClCFClBr$, $BrCF_2CF_2CF_2Br$, $BrCF_2CFBrOCF_3$, 1-bromo-2-iodoperfluoroethane, 1-bromo-3-iodoperfluoropropane, 1-bromo-4-iodoperfluorobutane, 2-bromo-3-iodoperfluorobutane, 3-bromo-4-iodoperfluorobutene-1, 2-bromo-4-iodoperfluorobutene-1, substitution products having a substituent at various positions such as monoiodomonobromo-substituted product, diiodomonobromo-substituted product, monoiododibromo-substituted product and (2-iodoethyl)- and (2-bromoethyl)-substituted products of benzene, and the like.

Among them, from the viewpoint of polymerization reactivity, crosslinking reactivity and availability, 1,4-diiodoperfluorobutane and diiodomethane are preferably used.

Examples of other copolymerizable iodine-containing monomer are, for instance, iodinated perfluoro(vinyl ethers) such as perfluoro(6,6-dihydro-6-ido-3-oxa-1-hexene) and perfluoro(5-ido-3-oxa-1-pentene) which are described in JP-B-5-63482 and JP-A-62-12734.

In case of the emulsion polymerization, a polymerization temperature and time may be from 5° to 150°C and from 0.5 to 100 hours, respectively.

Also in case of the emulsion polymerization, a polymerization product is usually separated and collected by a coagulation method. In the coagulation step, the coagulation may be carried out by so-called salting by using a metal salt or in case of avoiding mixing of a metal, by adding an acid.

The fluorine-containing elastomeric terpolymer of the present invention may have the following physical properties.

Number average molecular weight (based on polystyrene): 5,000 to 20 500,000.

Weight average molecular weight: 10,000 to 4,000,000.

Glass transition temperature: -20°C to +10°C.

In preparation of the fluorine-containing elastomeric terpolymer of the present invention, other monomers can be further 25 copolymerized to give a polymer comprising four or more monomers.

Examples of the copolymerizable monomer are, for instance, tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE),

perfluoro(alkyl vinyl ether) (PAVE), trifluoroethylene, vinyl fluoride, propylene, and the like. Particularly TFE and CTFE are preferable from the point that a productivity can be enhanced. A proportion of those other copolymerizable monomers is up to 10 % by mole, preferably from 5 1 to 5 % by mole.

Further the present invention relates to the composition for vulcanization which comprises the above-mentioned fluorine-containing elastomeric terpolymer, a vulcanizing agent and as the case demands, a vulcanization accelerator.

10 An adding amount of the vulcanizing agent may be selected optionally in the same range as usual depending on kind of the vulcanizing agent and components of the fluorine-containing terpolymer (the number of cure sites, etc.). The adding amount is usually from 0.5 to 5 parts by weight (hereinafter referred to as "part") based on 100 parts
15 of the terpolymer. Similarly an adding amount of the vulcanization accelerator may be selected in the same range as usual, and is usually from 0.2 to 10 parts based on 100 parts of the terpolymer.

As mentioned above, the fluorine-containing terpolymer of the present invention possesses enhanced amine resistance while 20 properties of a fluorine-containing rubber are maintained, and the terpolymer is an elastomer capable of polyol vulcanization which is advantageous in processing.

Therefore polyol vulcanization method is most preferable for the composition for vulcanization of the present invention while it 25 is a matter of course that peroxide vulcanization and polyamine vulcanization can be adopted.

As the vulcanizing agent for the polyol vulcanization method,

there can be used compounds which have been known as the vulcanizing agent for fluorine-containing rubbers. For example, polyhydroxy compounds, particularly aromatic polyhydroxy compounds can be used preferably. Examples thereof are, for instance, 2,2-bis(4-hydroxyphenyl)propane (so-called "bisphenol A"), 2,2-bis(4-hydroxyphenyl)perfluoropropane (so-called "bisphenol AF"), resorcin, 1,3-trihydroxybenzene, 1,7-dihydroxynaphthalene, 2,7-dihydroxynaphthalene, 1,6-dihydroxynaphthalene, dihydroxydiphenyl, 4,4'-dihydroxystilbene, 2,6-dihydroxyanthracene, hydroquinone, catechol, 2,2-bis(4-hydroxyphenyl)butane (so-called "bisphenol B"), 4,4-bis(4-hydroxyphenyl)valerate, 2,2-bis(4-hydroxyphenyl)tetrafluorodichloropropane, dihydroxydiphenylsulfone, 4,4'-dihydroxydiphenylketone, tri(4-hydroxyphenyl)methane, 3,3',5,5'-tetrachlorobisphenol A, 3,3',5,5'-tetrabromobisphenol A, alkali metal salt or alkali earth metal salt thereof, and the like. However when coagulation of the terpolymer is carried out by using an acid, it is preferable that the above-mentioned metal salts are not used.

As the vulcanization accelerator for the polyol vulcanization, there can be used onium compounds known as the vulcanization accelerator for the polyol vulcanization of fluorine-containing rubbers. Examples thereof are, for instance, ammonium compounds such as tertiary ammonium salt, phosphonium compounds such as tertiary phosphonium salt, oxonium compounds, sulfonium compounds, and the like. Particularly the tertiary ammonium salt and tertiary phosphonium salt are preferable.

Examples of the tertiary ammonium salt are, for instance,

8-methyl-1,8-diaza-bicyclo[5.4.0]-7-undeceniumchloride, 8-methyl-1,8-diaza-bicyclo[5.4.0]-7-undeceniumiodide, 8-methyl-1,8-diaza-bicyclo[5.4.0]-7-undeceniumhydroxide, 8-methyl-1,8-diaza-bicyclo[5.4.0]-7-undecenium-methylsulfate, 8-ethyl-1,8-diaza-
5 bicyclo[5.4.0]-7-undeceniumbromide, 8-propyl-1,8-diaza-bicyclo[5.4.0]-7-undeceniumbromide, 8-dodecyl-1,8-diaza-bicyclo[5.4.0]-7-undeceniumchloride, 8-dodecyl-1,8-diaza-bicyclo[5.4.0]-7-undeceniumhydroxide, 8-eicosyl-1,8-diaza-bicyclo[5.4.0]-7-undeceniumchloride, 8-tetracosyl-1,8-diaza-
10 bicyclo[5.4.0]-7-undeceniumchloride, 8-benzyl-1,8-diaza-bicyclo[5.4.0]-7-undeceniumchloride, 8-benzyl-1,8-diaza-bicyclo[5.4.0]-7-undeceniumhydroxide, 8-phenethyl-1,8-diaza-bicyclo[5.4.0]-7-undeceniumchloride, 8-(3-phenylpropyl)-1,8-diaza-bicyclo[5.4.0]-7-undeceniumchloride, and the like; phenyltrimethylammonium chloride,
15 phenyltrimethylammonium bromide, phenyltrimethylammoniumhydrogen sulfate, phenyltriethylammonium chloride, phenyltrioctylammonium bromide, and the like; 1,8-diazabicyclo[5.4.0]-7-undecenium octanoate, 1,8-diazabicyclo[5.4.0]-7-undecenium nonanoate, 1,8-diazabicyclo[5.4.0]-7-undecenium
20 decanoate, 1,6-diazabicyclo[4.3.0]-5-non enium octanoate, tetrabutylammonium octanoate, tetrabutylammonium nonanoate, trioctylmethylammonium octanoate, trioctylmethylammonium nonanoate, and the like; 1,8-diazabicyclo[5.4.0]-7-undecenium formate, 1,6-diazabicyclo[4.3.0]-5-non enium formate, tetrabutylammonium
25 formate, trioctylmethylammonium formate, and the like; tetrabutylammoniumhydrogen sulfate, tetramethylammoniumhydrogen sulfate, benzyltributylammoniumhydrogen sulfate,

trioctylmethylammoniumhydrogen sulfate, 1,8-diazabicyclo[5.4.0]-7-undecenium hydrogen sulfate, 8-methyl-1,8-diazabicyclo[5.4.0]-7-undecenium hydrogen sulfate, and the like. Among them, organic tertiary ammonium hydrogen sulfates such as
5 tetrabutylammoniumhydrogen sulfate are preferable from the viewpoint of enabling vulcanizability to be enhanced.

Examples of the tertiary phosphonium salt are, for instance, tetrabutylphosphonium chloride, benzyltriphenylphosphonium chloride, benzyltrimethylphosphonium chloride, benzyltributylphosphonium
10 chloride, tetrabutylphosphonium benzotriazole salt, tetrapropylphosphonium benzotriazole salt, triphenylbenzylphosphonium benzotriazole salt, and the like.

Further in order to enhance vulcanizability, for example, dimethyl sulfone, diethyl sulfone, dibutyl sulfone, methyl ethyl sulfone,
15 diphenyl sulfone, sulfolane, and the like; 1,8-diazabicyclo[5.4.0]-7-undecene, 1,5-diazabicyclo[4.3.0]-5-nonene, triethylamine, tributylamine, diphenylamine, ethyleneimine, piperidine, morpholine, pyridine, benzotriazole, p-dimethylaminopyridine, 1,4-diazabicyclo[2.2.2]octane, triphenyl phosphine, tributyl phosphine,
20 trioctyl phosphine, triphenyl phosphite, triethyl phosphite, triphenyl phosphate, tributyl phosphate, triphenyl phosphine oxide, trioctyl phosphine oxide, or the like may be added.

An adding amount of the polyol vulcanizing agent (for example, polyhydroxy compound) is usually from 0.5 to 5 parts,
25 preferably from 1 to 2 parts based on 100 parts of the terpolymer. An adding amount of the vulcanization accelerator (for example, onium compound) is usually from 0.2 to 10 parts, preferably from 0.5 to 5 parts

based on 100 parts of the terpolymer.

The polyol vulcanization can be carried out in the same manner as in conventional method. For example, there is a method of kneading with rolls the terpolymer of the present invention, a 5 vulcanizing agent and as the case demands, a vulcanization accelerator and further other optional additives, putting the mixture in a metal die, and carrying out primary vulcanization under pressure and then secondary vulcanization. For the kneading, an internal mixer, Banbury mixer, or the like can be used preferably. Generally conditions for the 10 primary vulcanization are a temperature of from 100° to 200°C, a time of from 10 to 180 minutes and a pressure of from about 2 MPa to about 10 MPa, and conditions for the secondary vulcanization are a temperature of from 150° to 300°C and a time of from about 30 minutes to about 30 hours.

15 One of the features of the composition for vulcanization of the present invention is that the polyol vulcanization can be carried out easily. As a result, excellent characteristics and rubber processability such as little contamination of a metal die, excellent heat resistance of an obtained vulcanized molded article and easy adhesion to a metal can 20 be obtained.

As mentioned above, the composition for vulcanization of the present invention can be subjected to peroxide vulcanizing and polyamine vulcanizing in addition to the polyol vulcanizing.

For the peroxide vulcanization, usually organic peroxides 25 which easily generate a peroxy radical in the presence of heat or an oxidation-reduction system are used preferably. Examples thereof are, for instance, 1,1-bis(t-butylperoxy)-3,5,5-trimethylcyclohexane, 2,5-

dimethylhexane-2,5-dihydro peroxide, di-t-butyl peroxide, t-butylcumyl peroxide, dicumyl peroxide, 2,5-dimethyl-2,5-bis(t-butylperoxy)hexane, α,α -bis(t-butylperoxy)-p-diisopropyl benzene, 2,5-dimethyl-2,5-di(t-butylperoxy)-hexine-3, benzoyl peroxide, t-butyl peroxybenzene, t-butyl 5 peroxybenzoate, 2,5-dimethyl-2,5-di(benzoylperoxy)-hexane, t-butyl peroxymaleate, t-butylperoxy isopropylcarbonate, and the like. Among them, dialkyl peroxides, particularly t-butyl peroxybenzoate, 2,5-dimethyl-2,5-di(t-butylperoxy)-hexane and dicumyl peroxide are preferable.

10 An adding amount of the organic peroxide may be optionally determined in consideration of an amount of an active -O-O- bond in the organic peroxide and a decomposition temperature thereof, and is usually from 0.05 to 10 parts, preferably from 1.0 to 5 parts based on 100 parts of the terpolymer.

15 In the peroxide vulcanization with the organic peroxide, curing (vulcanization) is accelerated remarkably by using a vulcanization aid (vulcanization accelerator). Examples of the vulcanization aid are those which have been used so far, for instance, triallyl cyanurate, triallyl isocyanurate, triacryl formal, triallyl trimellitate, N,N'-m-phenylenebismaleimide, dipropargyl terephthalate, 20 diallyl phthalate, tetraallyl terephthalateamide, triallyl phosphate, and the like. Particularly triallyl isocyanurate is preferable. An adding amount thereof is usually from 0.1 to 10 parts, preferably from 0.5 to 5 parts based on 100 parts of the terpolymer.

25 The peroxide vulcanization can be carried out in the same manner as in conventional method. For example, there is a method of kneading with rolls the terpolymer of the present invention, a

vulcanizing agent and as the case demands, a vulcanization accelerator and further other optional additives, putting the mixture in a metal die, and carrying out primary vulcanization under pressure and then secondary vulcanization. Generally conditions for the primary
5 vulcanization are a temperature of from 100° to 200°C, a time of from 5 to 60 minutes and a pressure of from about 2 MPa to about 10 MPa, and conditions for the secondary vulcanization are a temperature of from 150° to 300°C and a time of from about 30 minutes to about 30 hours.

A polyamine compound to be used for the polyamine
10 vulcanization not only acts as a vulcanizing agent but also improves mechanical properties of a vulcanized article (for example, strength at break, etc.). Examples thereof are, for instance, monoamines such as ethylamine, propylamine, butylamine, benzylamine, allylamine, n-amylamine and ethanolamine; diamines such as ethylenediamine,
15 trimethylenediamine, tetramethylenediamine, hexamethylenediamine and 3,9-bis(3-aminopropyl)-2,4,8,10-tetraoxaspiro[5,5]undecane; and polyamines such as diethylenetriamine, triethylenetetramine, tetraethylenepentamine and pentaethylenehexamine. Particularly
amine compounds having two or more end amino groups are preferable.
20 An adding amount thereof is usually from 0.5 to 10 parts, preferably from 1 to 5 parts based on 100 parts of the terpolymer.

The polyamine vulcanization can be carried out in the same manner as in conventional method. For example, there is a method of kneading with rolls the terpolymer of the present invention, a
25 vulcanizing agent and as the case demands, a vulcanization accelerator and further other optional additives, putting the mixture in a metal die, and carrying out primary vulcanization under pressure and then

secondary vulcanization. Generally conditions for the primary vulcanization are a temperature of from 100° to 200°C, a time of from 5 to 120 minutes and a pressure of from about 2 MPa to about 10 MPa, and conditions for the secondary vulcanization are a temperature of 5 from 150° to 300°C and a time of from about 30 minutes to about 30 hours.

As mentioned above, the vulcanized molded article of the present invention possesses excellent heat resistance, oil resistance, amine resistance and chemical resistance, and can be used for various 10 parts in automotive industry, airplane industry and semiconductor industry. The molded article is suitably used particularly for parts for oil seal, for example, hose and oil seal for engine oil of automotive by making the best use of its excellent heat resistance, oil resistance and amine resistance. Examples of other suitable applications are 15 mentioned below.

Applications of molded articles:

Packing, O-ring, hose, other sealing material, diaphragm and valve having amine resistance, oil resistance, chemical resistance, steam resistance and weather resistance in transportation means such as 20 automotive, ship and airplane; similar packing, O-ring, sealing material, diaphragm, valve, hose, roll and tube in chemical plant; similar packing, O-ring, hose, sealing material, belt, diaphragm, valve, roll and tube in foods plant and foods processing machine (including domestic appliances); similar packing, O-ring, hose, sealing material, diaphragm, 25 valve and tube in nuclear plant; similar packing, O-ring, hose, sealing material, diaphragm, valve, roll, tube, mandrel, cable, flexible joint, belt, rubber plate, weatherstrip, roll blade for PPC copying machine, etc. in

general industrial parts.

More concretely there are the following applications.

(i) Automotive applications

The molded article of the present invention can be used for
5 the above-mentioned car-related applications, more concretely for the
following applications.

(1) For sealing

- 10 Crank shaft seal
- Gear box seal
- Power piston packing
- Cylinder liner seal
- Valve stem seal
- Front pump seal for automatic transmission
- Rear axle pinion seal
- 15 Gasket for universal joint
- Pinion seal for speed meter
- Piston cup for foot brake
- O-ring and oil seal for torque transmission
- Seal for after-burner for exhaust gas
- 20 Bearing seal
- Differential seal
- Wheel bearing seal

(2) For hose

- 25 EGR tube
- Twin-carburetor tube

(3) For diaphragm

- Diaphragm for sensor of carburetor

(4) Others

Vibration-proof rubber (engine mount, exhaust system, etc.)

Hose for after burner

(ii) Applications in chemical industries

5 (1) For sealing

Seals for pump, flow meter and pipe for chemicals

Seal for heat exchanger

Packing of glass cooler for sulfuric acid manufacturing equipment

10 Seals for sprinkler and transfer pump for agricultural chemicals

Seal for gas pipe

Seal for plating solution

Packing for high temperature vacuum dryer

15 Roll seal of belt for paper making

Seal for fuel battery

Joint seal for air duct

(2) For roll

Roll having trichlene resistance (for dyeing of fiber)

20 (3) Other applications

Acid resistant hose (for concentrated sulfuric acid)

Packing for joint of tubes for gas chromatograph and pH meter

Chlorine gas transfer hose

25 Rainwater drain hoses for benzene and toluene reservoir tanks

Seal, tube, diaphragm and valve parts for analyzer and

physical and chemical appliances

(iii) Applications in industrial machinery

(1) For sealing

- Seals for hydraulic and lubricating machine
- 5 Bearing seal
- Seal for dry copying machine
- Seals for window, etc. of dry cleaner
- Seal for equipment for concentrating uranium hexafluoride
- 10 Seal (vacuum) valve for cyclotron
- Seal for automatic packaging machine

(2) Other applications

- Rolls, scraper, tube and valve parts for printing equipment
- Rolls, scraper, tube and valve parts for coating equipment
- Ink tube, roll and belt for printer
- 15 Belt and rolls for dry copying machine
- Diaphragms for pumps for analyzing sulfurous acid gas and chlorine gas in the air (environmental pollution-related meters)
- Rolls and belt for printer
- 20 Squeeze rolls for pickling

(iv) Airplane applications

- Valve stem seal for jet engine
- Fuel feeding hose, gasket and O-ring
- Rotating shaft seal
- 25 Gasket for hydraulic equipment
- Seal for fire wall

(v) Ship applications

Stern seal for screw propeller shaft

Suction and exhaust valve stem seals for diesel engine

Valve seal for butterfly valve

Stem seal for butterfly valve

5 (vi) Food and medicine applications

Seal for plate heat exchanger

Solenoid valve seal for vending machine

Plugs for chemicals

(vii) Electrical applications

10 Insulation oil cap for a train of the Shikansen line

Venting seal for liquid ring transformer

Jacket for oil well cable

Further the molded article of the present invention can be used for O-ring, sealing material, hose, tube, diaphragm, roll, lining and coating in equipment for producing semiconductor, liquid crystal panel, plasma display panel, plasma address liquid crystal panel, field emission display panel, substrate for solar battery, etc., for example, CVD equipment, etching equipment, oxidation/diffusion equipment, sputtering equipment, ashing equipment, ion implantation equipment, exhausting equipment, and the like which require plasma resistance; O-ring, sealing material, hose, tube, diaphragm and roll in wet etcher, cleaning equipment, pipes for chemicals, gas pipes, and the like which require chemical resistance; and further O-ring, sealing material, hose, tube, diaphragm and roll to be used on parts of the mentioned equipment which are required to be free from dust and metal.

Examples of other applications where chemical resistance is required are O-ring, sealing material, hose, tube, diaphragm of pump

and wafer transferring rolls for resist developing solution, releasing solution and wafer cleaning solution in production equipment for semiconductor, liquid crystal panel, plasma display panel, etc.

The present invention is then explained concretely by means
5 of examples, but is not limited thereto.

EXAMPLE 1

A 3-liter stainless steel autoclave was charged with 1.5 liter of ion-exchanged water and 150.0 g of ammonium perfluorooctanoate and
10 the atmosphere inside the autoclave was replaced with nitrogen gas sufficiently. The autoclave was then charged with 500.0 g of hexafluoropropylene (HFP) in a vacuum state, the inside temperature of the autoclave was increased to 65°C, and a gas mixture of ethylene/vinylidene fluoride (VdF) (50/50 % by mole) was introduced
15 under pressure until the pressure inside the autoclave was increased to 30 kg/cm²G. While stirring a system with an electromagnetic stirrer, the system was allowed to stand until the inside pressure became constant. Then 0.5 g of ammonium persulfate (APS) in an aqueous solution was introduced with pressurized nitrogen gas to initiate a
20 reaction. Since the inside pressure was decreased with the advance of the reaction, the pressure reduction was made up for by adding the gas mixture of ethylene/VdF (50/50 % by mole). The reaction was continued for 26.6 hours at constant pressure and temperature. APS was added in a total amount of 2.5 g until completion of the reaction.

25 After the completion of the reaction, the remaining monomer was released into the air. The obtained emulsified dispersion was coagulated with an aqueous solution of calcium chloride and then after

washing with ion-exchanged water, dried at 120°C until a constant value was obtained, and 529 g of an elastomeric polymerization product was obtained.

Components, molecular weight and glass transition temperature of the polymerization product were determined by analyzing methods of $^1\text{H-NMR}$, elementary analysis, GPC and DSC. As a result, the product was a terpolymer of 40.0 % by mole of ethylene unit, 38.9 % by mole of HFP unit and 21.1 % by mole of VdF unit, a number average molecular weight (based on polystyrene) was 85,000, a weight average molecular weight was 2,200,000 and a glass transition temperature was -1.7°C.

EXAMPLE 2

A 3-liter stainless steel autoclave was charged with 1.5 liter of ion-exchanged water and 75.0 g of ammonium perfluorooctanoate and the atmosphere inside the autoclave was replaced with nitrogen gas sufficiently. The autoclave was then charged with 500.0 g of hexafluoropropylene (HFP) in a vacuum state, the inside temperature of the autoclave was increased to 50°C, and a gas mixture of ethylene/vinylidene fluoride (VdF) (50/50 % by mole) was introduced under pressure until the pressure inside the autoclave was increased to 2.94 MPa·G (30 kgf/cm²G). While stirring a system with an electromagnetic stirrer, the system was allowed to stand until the inside pressure became constant. Then 30.0 g of an aqueous solution of 10 % by weight of ammonium persulfate (APS) was introduced under pressure with a plunger pump to initiate a reaction. Since the inside pressure was decreased with the advance of the reaction, the pressure reduction

was made up for by adding the gas mixture of ethylene/VdF (50/50 % by mole). The reaction was continued for 72 hours at constant pressure and temperature. The aqueous solution of APS was added in a total amount of 139.0 g until completion of the reaction.

5 After the completion of the reaction, the remaining monomer was released into the air. The obtained emulsified dispersion was coagulated with an aqueous solution of calcium chloride and then after washing with ion-exchanged water, dried at 120°C until a constant value was obtained, and 460 g of an elastomeric polymerization product was
10 obtained.

As a result of analysis of the polymerization product made in the same manner as in Example 1, the product was a terpolymer of 47.2 % by mole of ethylene unit, 34.9 % by mole of HFP unit and 17.9 % by mole of VdF unit, a number average molecular weight (based on
15 polystyrene) was 50,000, a weight average molecular weight was 470,000 and a glass transition temperature was -4.7°C.

EXAMPLES 3 and 4

The elastomeric terpolymers prepared in Examples 1 and 2,
20 respectively, a carbon black, a peroxide vulcanizing agent and a vulcanization accelerator were mixed in amounts shown in Table 1 and kneaded by using an open roll at ordinary temperature. Any of the components was good in adhesion to the roll and easy to knead. The obtained rubber compound was put in a metal die, and subjected to
25 primary vulcanizing by press vulcanization and then secondary vulcanizing by vulcanization in an oven to give a vulcanized molded article.

Physical properties in normal state, oil resistance, amine resistance and heat resistance of the obtained vulcanized molded article were measured by the following methods. The results are shown in Table 1.

5 (Physical properties in normal state)

According to JIS K6301, JIS-A hardness (Hs), 100 % modulus (M100), tensile strength at break (TB) and tensile elongation at break (EB) are measured.

(Resistance to engine oil)

10 A change in Hs (degree), a change in TB (%), a change in EB (%) and a change in volume (%) after dipping in ASTM SF105G oil at 175°C for 168 hours are measured.

(Heat resistance)

15 A change in Hs (degree), a change in TB (%) and a change in EB (%) after exposing in the air at 230°C for 70 hours are measured.

(Amine resistance)

A change in Hs (degree), a change in TB (%), a change in EB (%) and a change in volume (%) after dipping in ethylenediamine at room temperature for 16 hours are measured.

20 In Table 1, each of additives represents the followings.

PERBUTYL Z: Peroxide vulcanizing agent available from NOF CORPORATION

TAIC: Triallyl isocyanate (vulcanization accelerator available from Nippon Kasei Chemical Co., Ltd.)

25 MA150: MgO (acid acceptor available from Kyowa Kagaku Kabushiki Kaisha

Thermax N-990: Carbon black available from Cancarb Co., Ltd.

TABLE 1

| | Ex. 3 | Ex. 4 |
|---|-------------|-------------|
| Composition for vulcanization (part by weight) | | |
| Elastomeric terpolymer | 100 (Ex. 1) | 100 (Ex. 2) |
| PERBUTYL Z | 3.7 | 3.7 |
| TAIC | 2.5 | 2.5 |
| MA150 | 3 | 3 |
| Thermax N-990 | 30 | 30 |
| Physical properties of vulcanized molded article | | |
| Physical properties in normal state | | |
| Hs (JIS A) | 72 | 72 |
| M100 (MPa) | 4.7 | 5.1 |
| TB (MPa) | 12.7 | 16.7 |
| EB (%) | 220 | 250 |
| Engine oil resistance | | |
| Change in Hs (degree) | - | -3 |
| Change in TB (%) | - | -36.7 |
| Change in EB (%) | - | -35.3 |
| Change in volume (%) | - | 3.7 |
| Heat resistance | | |
| Change in Hs (degree) | - | 6 |
| Change in TB (%) | - | -19.8 |
| Change in EB (%) | - | -37.2 |
| Amine resistance | | |
| Change in Hs (degree) | 0 | -3 |
| Change in TB (%) | 2.3 | -1.8 |
| Change in EB (%) | -6.2 | 0.2 |
| Change in volume (%) | 3.1 | 2.8 |

EXAMPLES 5 and 6

The elastomeric terpolymers prepared in Examples 1 and 2, respectively, a carbon black, a polyol vulcanizing agent and a vulcanization accelerator were mixed in amounts shown in Table 2 and 5 kneaded by using an open roll at ordinary temperature. Any of the components was good in adhesion to the roll and easy to knead. The obtained rubber compound was put in a metal die, and subjected to primary vulcanizing by press vulcanization and then secondary vulcanizing by vulcanization in an oven to give a vulcanized molded 10 article.

Physical properties in normal state and heat resistance of the obtained vulcanized molded article were measured in the same manner as in Example 4. The results are shown in Table 2.

In Table 2, each of additives represents the followings.

15 Bisphenol AF: Polyol vulcanizing agent
TBAHS: Tetrabutylammoniumhydrogen sulfate (vulcanization
accelerator)
Ca(OH)₂: available from Ohmi Kagaku Kabushiki Kaisha

TABLE 2

| | Ex. 5 | Ex. 6 |
|---|-------------|-------------|
| Composition for vulcanization (part by weight) | | |
| Elastomeric terpolymer | 100 (Ex. 1) | 100 (Ex. 2) |
| Bisphenol AF | 1.5 | 1.5 |
| TBAHS | 0.7 | 0.7 |
| Ca(OH) ₂ | 6 | 6 |
| MA150 | 3 | 3 |
| Thermax N-990 | 30 | 30 |
| Physical properties of vulcanized molded article | | |
| Physical properties in normal state | | |
| Hs (JIS A) | 77 | 80 |
| M100 (MPa) | 4.2 | 7.8 |
| TB (MPa) | 13.4 | 13.9 |
| EB (%) | 280 | 180 |
| Heat resistance | | |
| Change in Hs (degree) | - | 0 |
| Change in TB (%) | - | -11.0 |
| Change in EB (%) | - | -10.4 |

EXAMPLES 7 to 14

A 100-ml stainless steel autoclave was charged with 50 ml of
5 ion-exchanged water and 2.5 g of ammonium perfluorooctanoate and
the atmosphere inside the autoclave was replaced with nitrogen gas
sufficiently. The autoclave was then charged under pressure in a
vacuum state with hexafluoropropylene (HFP), ethylene and vinylidene
fluoride (VdF) in amounts shown in Table 3. Then 1.5 g of an aqueous
10 solution of 10 % by weight of ammonium persulfate (APS) was
introduced under pressure with a plunger pump to initiate a reaction.

During the reaction the autoclave was set in a shaking machine provided with temperature control means, and was subjected to shaking for two hours at intervals of 125 times per minute while the inside temperature was maintained at 65°C.

5 After completion of the reaction, coagulation, washing and drying were carried out in the same manner as in Example 1, and elastomeric polymerization products were obtained in amounts shown in Table 3.

The obtained products were analyzed in the same manner as
10 in Example 1. The results are shown in Table 3.

TABLE 3

| | Ex. 7 | Ex. 8 | Ex. 9 | Ex. 10 | Ex. 11 | Ex. 12 | Ex. 13 | Ex. 14 |
|---|--------|--------|--------|--------|--------|--------|--------|--------|
| Adding amount (g) | | | | | | | | |
| HFP | 13.5 | 13.4 | 10.7 | 10.8 | 8.1 | 8.1 | 5.5 | 5.5 |
| Ethylene | 1.0 | 1.0 | 0.5 | 0.5 | 0.6 | 1.9 | 0.6 | 2.0 |
| VdF | 3.5 | 4.5 | 4.7 | 5.8 | 7.0 | 4.0 | 7.6 | 4.6 |
| Components of terpolymer (% by mole) | | | | | | | | |
| HFP | 38.9 | 37.6 | 36.3 | 33.9 | 32.4 | 34.5 | 27.9 | 31.1 |
| Ethylene | 52.0 | 49.5 | 45.9 | 36.3 | 43.2 | 57.1 | 40.0 | 59.3 |
| VdF | 9.1 | 13.0 | 17.9 | 29.8 | 24.4 | 8.4 | 32.2 | 9.6 |
| Yield (g) | 0.9 | 0.9 | 0.8 | 1.2 | 0.7 | 0.7 | 0.6 | 0.5 |
| Molecular weight of terpolymer | | | | | | | | |
| Number average | 22,000 | 23,000 | 22,000 | 35,000 | 13,000 | 12,000 | 12,000 | 9,000 |
| Weight average | 45,000 | 45,000 | 43,000 | 67,000 | 33,000 | 28,000 | 29,000 | 21,000 |
| Glass transition temperature (°C) | -6.0 | -6.5 | -5.8 | -5.6 | -7.5 | -9.0 | -10.0 | -12.7 |

INDUSTRIAL APPLICABILITY

According to the present invention, a fluorine-containing copolymer which can be subjected to polyol vulcanization and has necessary and sufficient amine resistance while maintaining heat 5 resistance, oil resistance and chemical resistance nearly equal to those of conventional fluorine-containing rubbers can be provided, and a vulcanized molded article suitable, for example, as an oil seal and hose for engine oil, ATF and differential gear oil can be provided.

CLAIMS

1. (Amended) A fluorine-containing elastomeric terpolymer of 30 to 85 % by mole of ethylene unit, 14.9 to 45 % by mole of hexafluoropropylene unit and 0.1 to 25 % by mole of vinylidene fluoride unit (excluding a composition of 35 % by mole of ethylene unit, 40 % by mole of hexafluoropropylene unit and 25 % by mole of vinylidene fluoride unit).

2. (Deleted).

3. (Deleted).

4. (Deleted).

5. (Amended) The fluorine-containing elastomeric terpolymer of Claim 1, wherein a proportion of vinylidene fluoride unit is from 5 to 25 % by mole.

6. (Deleted).

7. (Deleted).

8. The fluorine-containing elastomeric terpolymer of Claim 1, wherein the terpolymer contains more than 65 % by mole and 85 % by mole or less of ethylene unit, 14.9 to 35 % by mole of hexafluoropropylene unit and 0.1 to 20 % by mole of vinylidene fluoride unit.

9. (Amended) The fluorine-containing elastomeric terpolymer of any of Claims 1, 5 and 8, wherein a number average molecular weight of the terpolymer is from 5,000 to 500,000 based on polystyrene.

10. (Amended) A composition for vulcanization which comprises the fluorine-containing elastomeric terpolymer of any of Claims 1, 5, 8 and 9 and a vulcanizing agent.

11. The composition of Claim 10 which contains a vulcanization accelerator.

12 The composition of Claim 10 or 11, wherein the vulcanizing agent is a polyol vulcanizing agent.

13. A vulcanized molded article produced by molding and vulcanizing the composition for vulcanization of any of Claims 10 to 12.

14. The vulcanized molded article of Claim 13 which is used for parts for oil seal.

Declaration and Power of Attorney for Patent Application

特許出願宣言書及び委任状

Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者であると（下記の名称が複数の場合）信じています。

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

FLUORINE-CONTAINING ELASTOMER AND

VULCANIZED MOLDED ARTICLE

上記発明の明細書（下記の欄でx印がついていない場合は、本書に添付）は、

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and was amended on _____
(if applicable)

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

私は、連邦規則法典第37編第1条56項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56.

Japanese Language Declaration

日本語宣言

私は、米国法典第35編119条(a)-(d)項又は365条(b)項に基づき下記の、米国以外の国の少なくとも一ヵ国を指定している特許協力条約365(a)項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

Prior foreign application(s) 外国での先行出願

| | |
|---------------------------------|----------------------------|
| 183676/1999 (Number) (番号) | Japan (Country) (国名) |
| 2000-86667 (Number) (番号) | Japan (Country) (国名) |
| (Number) (番号) | (Country) (国名) |

私は、第35編米国法典119条(e)項に基いて下記の米国特許出願規定に記載された権利をここに主張いたします。

| | |
|-----------------------------|------------------------|
| (Application No.) (出願番号) | (Filing Date) (出願日) |
|-----------------------------|------------------------|

私は、下記の米国法典第35編120条に基いて下記の米国特許出願に記載された権利、又は米国を指定している特許協力条約365条(c)に基づく権利をここに主張します。また、本出願の各請求範囲の内容が米国法典第35編112条第1項又は特許協力条約で規定された方法で先行する米国特許出願に開示されていない限り、その先行米国出願書提出日以降で本出願書の日本国内または特許協力条約国際提出までの期間中に入手された、連邦規則法典第37編1条56項で定義された特許資格の有無に関する重要な情報について開示義務があることを認識しています。

| | |
|-----------------------------|------------------------|
| (Application No.) (出願番号) | (Filing Date) (出願日) |
|-----------------------------|------------------------|

私は、私自身の知識に基づいて本宣言書中で私が行なう表明が真実であり、かつ私の入手した情報と私の信じるところに基づく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行なえば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby claim foreign priority under Title 35, United States Code, § 119(a)-(d) or § 365 (b) of any foreign application(s) for patent or inventor's certificate, or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Claimed 優先権の主張

| | |
|--|--|
| 29/6/1999 (Day/Month/Year Filed) (出願年月日) | <input checked="" type="checkbox"/> <input type="checkbox"/> Yes No ありなし |
| 27/3/2000 (Day/Month/Year Filed) (出願年月日) | <input checked="" type="checkbox"/> <input type="checkbox"/> Yes No ありなし |
| (Day/Month/Year Filed) (出願年月日) | <input type="checkbox"/> <input checked="" type="checkbox"/> Yes No ありなし |

I hereby claim the benefit under Title 35, United States Code, § 119(e) of any United States provisional application(s) listed below.

| | |
|-----------------------------|------------------------|
| (Application No.) (出願番号) | (Filing Date) (出願日) |
|-----------------------------|------------------------|

I hereby claim the benefit under Title 35, United States Code, § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code, § 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

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| (Status)(patented, pending, abandoned) (現況：特許許可済、係属中、放棄済) |
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| (Status)(patented, pending, abandoned) (現況：特許許可済、係属中、放棄済) |
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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Japanese Language Declaration

日本語宣言

委任状： 私は下記の発明者として、本出願に関する一切の手続を米特許商標局に対して遂行する弁護士または代理人として、下記の者を指名いたします。（弁護士、または代理人の氏名及び登録番号を明記のこと）

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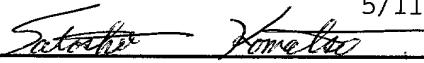
| | | |
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| 発明者の署名 | Inventor's signature | Date |
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（第三以降の共同発明者についても同様に記載し、署名をすること）

(Supply similar information and signature for third and subsequent joint inventors.)

Japanese Language Declaration

日本語宣言

| | | | |
|---------------------|----|--|--|
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| 同第三発明者の署名 | 日付 | Third inventor's signature | Date 5/11/2001 |
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| 同第四発明者の署名 | 日付 | Fourth inventor's signature | Date  5/11/2001 |
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| 同第五発明者の署名 | 日付 | Fifth inventor's signature | Date |
| 住所 | | Residence | |
| 国籍 | | Citizenship | |
| 郵便の宛先 | | Post office address | |
| 第六の共同発明者の氏名（該当する場合） | | Full name of sixth joint inventor, if any | |
| 同第六発明者の署名 | 日付 | Sixth inventor's signature | Date |
| 住所 | | Residence | |
| 国籍 | | Citizenship | |
| 郵便の宛先 | | Post office address | |